On a biphononic origin of the 1125 cm^{-1} absorption band in cuprous oxide

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We report on the IR spectroscopic studies in both reflection ($50-900$ cm^{-1}) and transmission ($900-3000$ cm^{-1}) mode of the vibration spectrum of the cuprous oxide. A detailed analysis based on a comparison of the temperature dependences of the absorption band at $\simeq$1125 cm^{-1} and of IR and Raman active fundamental vibrations results in assignment of the former to a biphonon.

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I. INTRODUCTION

Cuprous oxide (Cu_2O) has been studied for many years, mainly because of its very rich electronic spectrum showing a large number of excitonic structures associated with quadrupole and dipole transitions and phonon-assisted dipole transitions [1,2,3]. It serves also as a model object for investigation of nonequilibrium phenomena in electronic and excitonic systems [4]. Considerable attention has been paid to the phonon spectrum as well. Despite numerous infrared and Raman studies the phonon spectrum of cuprous oxide is still not well understood. The main problem is that the observed number of bands is much larger than that deduced from the group theory. This fact lead the authors to interpret the spectra in terms of models involving nonstochiometry or impurity defects or multiphonon processes in light absorption (scattering). The most intriguing point in the IR spectrum concerns the absorption peaks at frequencies higher than 1000 cm^{-1}. The band at $\sim$1125 cm^{-1}, for instance, was assigned to the transitions between two different sets of exciton levels [5], i.e. between the so-called "yellow" and "green" exciton series [6,7,8]. It was supposed that during the IR measurements the sample is illuminated with white light resulting in a population of long-living excitonic states which could absorb the infrared quanta. In Ref. [9] the 1125 cm^{-1} feature was assigned to a fundamental lattice vibration, though no indications of such a high frequency fundamental vibration are available from inelastic neutron scattering studies [10] and lattice dynamics calculations [11]. Another possible explanation of the 1125 cm^{-1} band was given in Ref. [12], where it was assigned to silicon-like impurities. In Ref. [14] it was supposed that this band is due to multiphonon process. Thus, no convincing interpretation of the high frequency peak at $\sim$1125 cm^{-1} has been given so far.

Present study is aimed at the origin of the $\sim$1125 cm^{-1} feature in the absorption spectrum of Cu_2O. To exclude its electronic origin we examined an influence of laser illumination on the absorption band intensity at $\sim$1125 cm^{-1}. Comparative study of the temperature dependences of the peak frequency and the band halfwidth on one hand and those of the IR and Raman active fundamental vibrations on the other hand showed that the absorption band at $\sim$1125 cm^{-1} is of a one-particle nature. Its peak position possesses quite different temperature dependence than any simple combination of the fundamental vibration frequencies. Also the temperature dependence of the band halfwidth is dominated by participation of high frequency ($\omega \gtrsim 500 \quad cm^{-1}$) phonons in the corresponding anharmonic decay processes. Thus, the $\sim$1125 cm^{-1} feature can be assigned either to some sort of intrinsic defect or to a biphonon, i.e. bound state of two phonons splitted from the two-phonon band $\omega_0(k) + \omega_0(-k)$ [13]. Biphonon is a single particle excitation and, disregarding rather unlike defect origin of the 1125 cm^{-1} feature, it can account for the peculiarities of the high frequency absorption band.

II. EXPERIMENTAL

All the spectral measurements to be described were carried out with a Bruker 113v Fourier-transform spectrometer in the range 50$-$3000 cm^{-1} with a spectral resolution of 0.5 cm^{-1}. Reflectance measurements were made at an angle

of incidence 11° on a bulk single crystal of 3x3 mm^2 area while the transmission was measured on a 1.5x1.5 mm^2 single crystalline sample of 70 μ thickness. The samples were cut and polished from high quality naturally grown single crystal.

For the low temperature measurements the sample was mounted in a special holder in a helium flow cryostat with temperature control better than 0.5 K. The reflectivity data were transformed into a dielectric function via Kramers-Kronig transformation and the peak maxima and halfwidths of the spectra of $Im[\varepsilon(\omega)]$ and $Im[-\varepsilon^{-1}(\omega)]$ were analyzed.

III. RESULTS AND DISCUSSION

The general features of the IR reflectance spectrum of Cu_2O have been published by several authors [15,16]. It is well established that there are two allowed IR active phonons of F_{1u} symmetry with TO phonon frequencies $\omega_{TO1} \simeq 150$ cm^{-1} and $\omega_{TO2} \simeq 605$ cm^{-1}. The assignments of the absorption peaks have been also given [17,18]. All the assignments made so far were based on the symmetry considerations when concerning the fundamental modes (the isotope shift of oxygen was also used in the assignment of the $\simeq 605$ cm^{-1} IR band [9]) and also simple combinations of the fundamental mode frequencies were applied to multiphonon peaks. The symmetry arguments for the latter ones are, however, not so strong as for the fundamental vibrations. A weaker intensity of multiphonon bands can be caused either by a small dipole moment for dipole allowed combinations of phonons or by a large electric quadrupole moment for dipole forbidden combinations. Additionally, the frequency of the multiphonon absorption band is not necessary exactly equal to a combination of phonon frequencies at the Γ point of the Brillouin zone. Thus, the assignment of a relatively weak IR band might be rather ambiguous. To make it more convincing one can consider the temperature dependent spectra assuming that the multiphonon peaks are combined from one and the same phonons over a wide temperature range. Then, obviously, the multiphonon peak position must follow the combination of those of the constituent phonons when heating or cooling the sample. The integrated intensity of the multiphonon peaks is generally also temperature dependent, but its determination is usually not of sufficiently high accuracy and can not be used as an argument in favor or against their multiphonon nature.

A. The 1125 cm^{-1} feature is not of electronic origin

Fig.1 presents the spectra of optical density obtained from the transmittance measured at various temperatures. The well pronounced and well separated absorption band at $\omega_B \simeq$1125 cm^{-1} (at T=295 K) is of our specific interest. The band shows a clear red shift and broadening with increasing temperature. Its peak position and halfwidth are plotted in Figs.2 and 3 respectively. There are also a number of overlapping bands at lower frequencies the parameters of which are not presented because of the low accuracy in their determination. By open circles we show in Fig.1 also the optical density of the sample illuminated by an Ar$^+$ cw laser (λ = 514 nm) with power about 1 W focused on 2 mm^2 at a nominal sample temperature of 10 K. Obviously the electronic excitation efficiency for the illumination conditions used is many orders in magnitude higher than that for illumination during the ordinary IR measurements and should result in a remarkable change of the ω_B band intensity if it is of the electronic origin discussed in [5]. Actually one sees from Fig.1 that the illumination results only in a small red shift and a broadening of the band just by the sample heating effect. No indications of absorption related to transitions between excitonic level is observed. The small peaks at $\simeq$1000 cm^{-1} and $\simeq$1250 cm^{-1} (curve 4 in Fig.1) remain unchanged after switching off the illumination suggesting some sort of persistent photoinduced origin. Together with the isotope shift of the frequency ω_B [9] our data give strong evidence for a *pure vibrational nature* of the band under discussion.

B. The 1125 cm^{-1} feature is not a multiphonon band

To answer the question about the multiphonon nature of the ω_B band we measured the temperature dependent reflectance spectrum (see Fig.4). The shifts of the TO and LO phonon frequencies obtained via Kramers-Kronig transformation from the reflectance spectra are shown in Fig.5. The frequency shift of the Raman line at $\omega_R \simeq$515 cm^{-1} [19] which in combination with ω_{TO2} could result in an absorption band at $\sim$1125 cm^{-1} is also presented. The experimental temperature dependences of the frequency shifts were fitted with the function

$$\Delta\omega(T) = \omega(T = 10K) - \omega(T) = \Delta_0 + C_1 \cdot T + C_2 \cdot T^2, \quad (1)$$

corresponding to the temperature dependences of the phonon band frequencies due to phonon decay processes and due to thermal expansion of the crystal lattice. Δ_0, C_1 and C_2 in (1) are fitting parameters. It turned out that the frequency shift of the ω_B band can be represented neither as the combination $\Delta\omega_B = \Delta \cdot (3 \cdot \omega_{LO1} + \omega_{LO2})$ [14] giving rise for electric quadrupole absorption nor as the $\Delta\omega_B = \Delta \cdot (\omega_R + \omega_{TO2})$ suggesting electric dipole absorption [20]. Moreover, no reasonable fit can be reached at all using Eq. (1) (see dotted line in Fig.2). Under a quite realistic assumption about the validity of the Eq. (1) over the whole Brillouin zone this fact means that the ω_B band is *not a simple multiphonon* one.

C. What is the origin of the ω_B band?

Since the ω_B band corresponds neither to an electronic transition nor to a multiphonon process one may turn back to its defect or impurity origin. It seems however quite unlikely that the relative intensity of the defect or impurity band compared to the fundamental absorption bands is nearly the same in a variety of samples from different sources and after different treatment. Therefore one should consider some sort of intrinsic defect, such as an oxygen atom (as evidenced by the isotope effect [9]) in an interstitial site (see also the argumentation in [17]). Even in this case, however, it is difficult to explain such a high frequency of an oxygen vibration which normally does not exceed 800 cm^{-1}.

The temperature dependences of the frequency shift $\Delta\omega_B(T)$ and the halfwidth $S_B(T)$ of the ω_B band can be described nearly perfectly by anharmonicity of third and fourth order [21] involving the high frequency phonons only suggesting a one-phonon origin of the ω_B band. Figs 2 and 3 (solid lines) demonstrate the fit obtained according to the expressions

$$\begin{gathered}\Delta\omega_B(T) = \omega_B(T=0) - \omega_B(T) \sim C_1 \cdot T + C_2 \cdot (n(\omega_{ph}, T) + \\ n(\omega_B(T=0) - \omega_{ph}, T)) + C_3 \cdot n(\omega_{ph}, T) \cdot (n(\omega_{ph}, T) + 1)\,,\end{gathered} \tag{2}$$

$$\begin{gathered}S_B(T) \sim S_B(T=0) \cdot (1 + n(\omega_{ph}, T) + n(\omega_B(T=0) - \omega_{ph}, T)) + \\ C_4 \cdot n(\omega_{ph}, T) \cdot (n(\omega_{ph}, T) + 1)\,,\end{gathered} \tag{3}$$

where $n(\omega, T) = (\exp(\hbar\omega/k_BT) - 1)^{-1}$ is phonon occupation number, $\omega_B(T=0) = 1153$ cm^{-1}, $S_B(T=0) \simeq 68$ cm^{-1}, $\omega_{ph} = \omega_B/2$. Constants C_1, C_2, C_3, and C_4 are fitting parameters. The thermal expansion effect is taken into account through the constant C_1. Dotted lines in Figs 2 and 3 show the best fits using Eq (1) for the $\Delta\omega_B(T)$ and Eq (3) with $\omega_{ph} \lesssim \omega_B/4$ for the $S_B(T)$, e.g. assuming that the ω_B band is of a two-phonon origin. Note, that the total number of the fit parameters in the latter case is even higher than that in the former one.

From the captures to Figs 2 and 3 one can see that the fourth order anharmonicity gives considerable contribution to both broadening and frequency shift of the 1153 cm^{-1} vibration. Now two important facts have to be pointed out: i) the value of the phonon frequency $\omega_{ph} \simeq 600$ cm^{-1} appears to be very close to ω_{TO2}; ii) the isotope effects for the ω_B and ω_{TO2} vibrations are nearly the same [9]. Both two facts can be naturally incorporated in the picture which considers the ω_B vibration as a bound state of two ω_{TO2} phonons, i.e. a biphonon. Indeed, fact i) means a much stronger interaction of the ω_B vibration with the ω_{TO2} phonons than with any other phonons just as a consequence of strong interaction between the ω_{TO2} phonons themselves resulting in the biphonon formation. The fact ii) gives evidence for a similarity between the eigenvectors of the ω_B and of the ω_{TO2} vibrations suggesting their common origin. Within the biphonon picture the IR activity of ω_B must be due to an electric quadrupole transition.

The biphonon picture described implies rather low binding energy $E_{bind} \simeq \hbar \cdot (2\omega_{TO2} - \omega_B) \simeq$100 cm^{-1} of the biphonon. This will result in a dissociation of the biphonons, i.e. in an additional broadening of the ω_B band at elevated temperatures caused by increasing interaction with phonons $\omega \simeq E_{bind}$, e.g. acoustic phonons. The process responsible for such a broadening would give the contribution

$$\Delta S_B(T) \sim \left[n(E_{bind}, T) \cdot (n(\omega_{TO2}, T) + 1)^2 - n^2(\omega_{TO2}, T) \cdot (n(E_{bind}, T) + 1) \right]. \tag{4}$$

As the ω_B band broadening does not contain any noticeable contribution of the low frequency phonons one may conclude that neither the process (4) nor those considered in [22] are not essential in our case.

IV. CONCLUSION

We performed IR spectroscopic studies both in reflection and transmission modes of the vibration spectrum of cuprous oxide. Detailed analysis of the temperature behavior of the resonance frequency and of the halfwidth of the

absorption band at $\omega_B \simeq$1125 cm^{-1} on one hand and of the frequencies of IR and Raman active phonons on the other hand result in the conclusion about a biphononic origin of the 1125 cm^{-1} vibration.

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Figure captures

Fig.1. Spectra od the optical density of cuprous oxide at temperature 10 K (1), 200 K (2), 295 K (3), and of 10 K with laser illumination (see text) (4).

Fig.2. Frequency shift $\Delta\omega$ of the $\omega_B \simeq 1125$ cm^{-1} absorption band in cuprous oxide versus temperature. (1) experimental data; (2) best fit with Eq. (1); (3) fit with Eq. (2) with $C_1 = 0.013$ cm$^{-1}/K$, $C_2 = 104.16$ cm^{-1}, $C_3 = 103.81$ cm^{-1}.

Fig.3. Halfwidth of the $\omega_B \simeq 1125\, cm^{-1}$ absorption band in cuprous oxide versus temperature. (1) experimental data; (2) fit with Eq (3) with $C_4 = 208.35$ cm^{-1}; (3) see text.

Fig.4. Reflectance spectra of cuprous oxide for various temperatures.

Fig.5. Frequency shifts $\Delta\omega$ of the fundamental vibrations in cuprous oxide versus temperature. (1) $\omega_{TO2} \simeq 605$ cm^{-1}; (2) $\omega_{TO1} \simeq 150$ cm^{-1}; (3) $\omega_{LO2} \simeq 660$ cm^{-1}; (4) $\omega_{LO2} \simeq 153$ cm^{-1}; (5) Raman line at $\omega_R \simeq 515$ cm^{-1} [19].

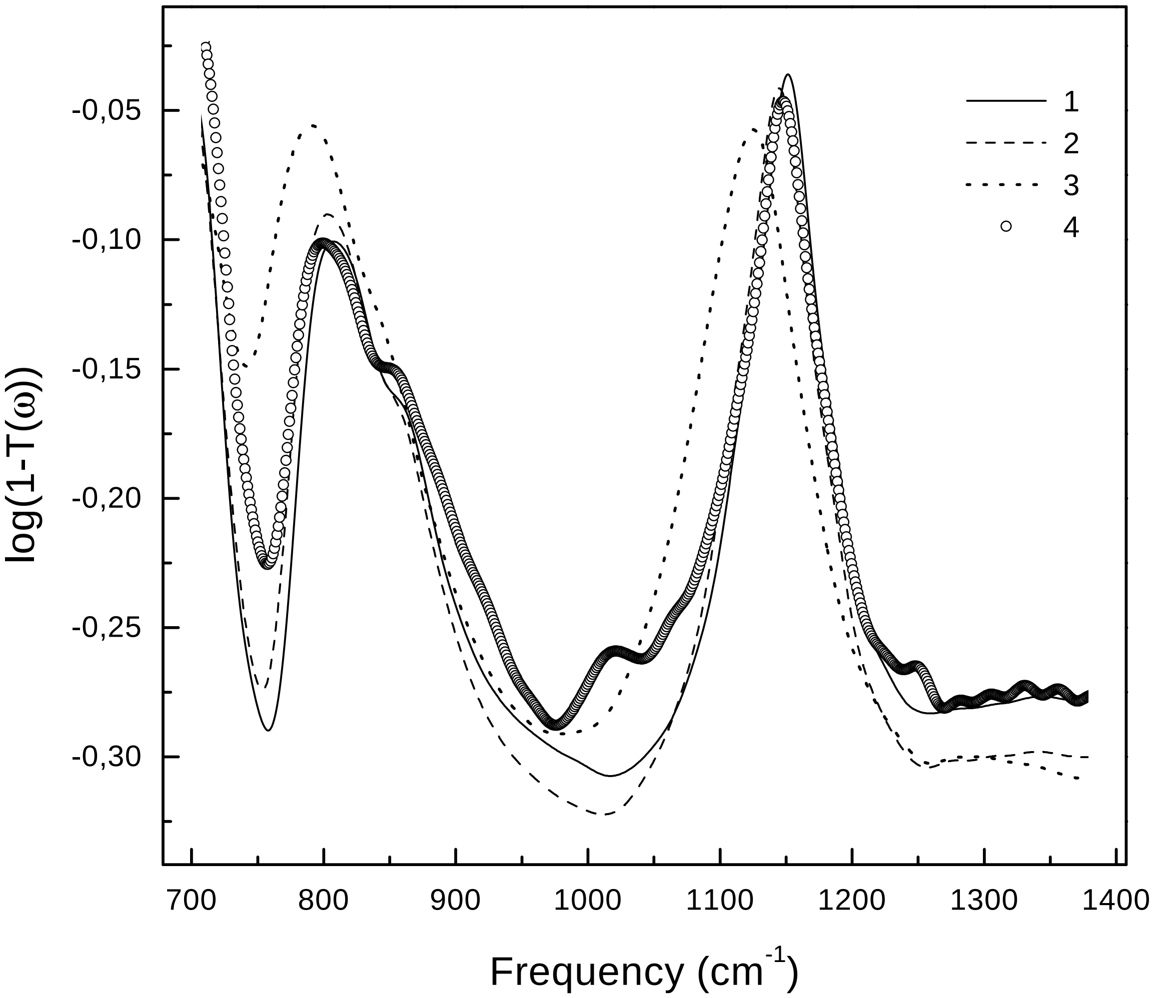


Fig.1. V.M.Burlakov et al., "On a biphononic origin of 1125 cm^{-1} absorption band in cuprous oxide"

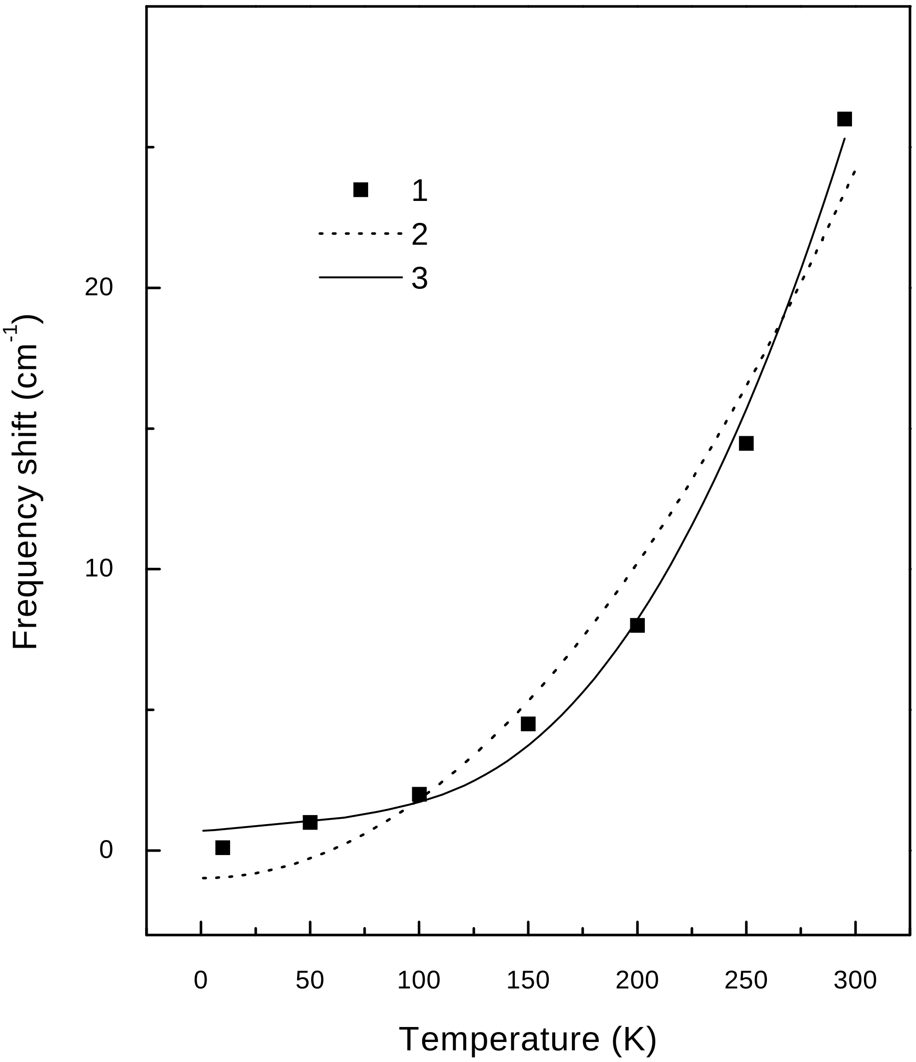
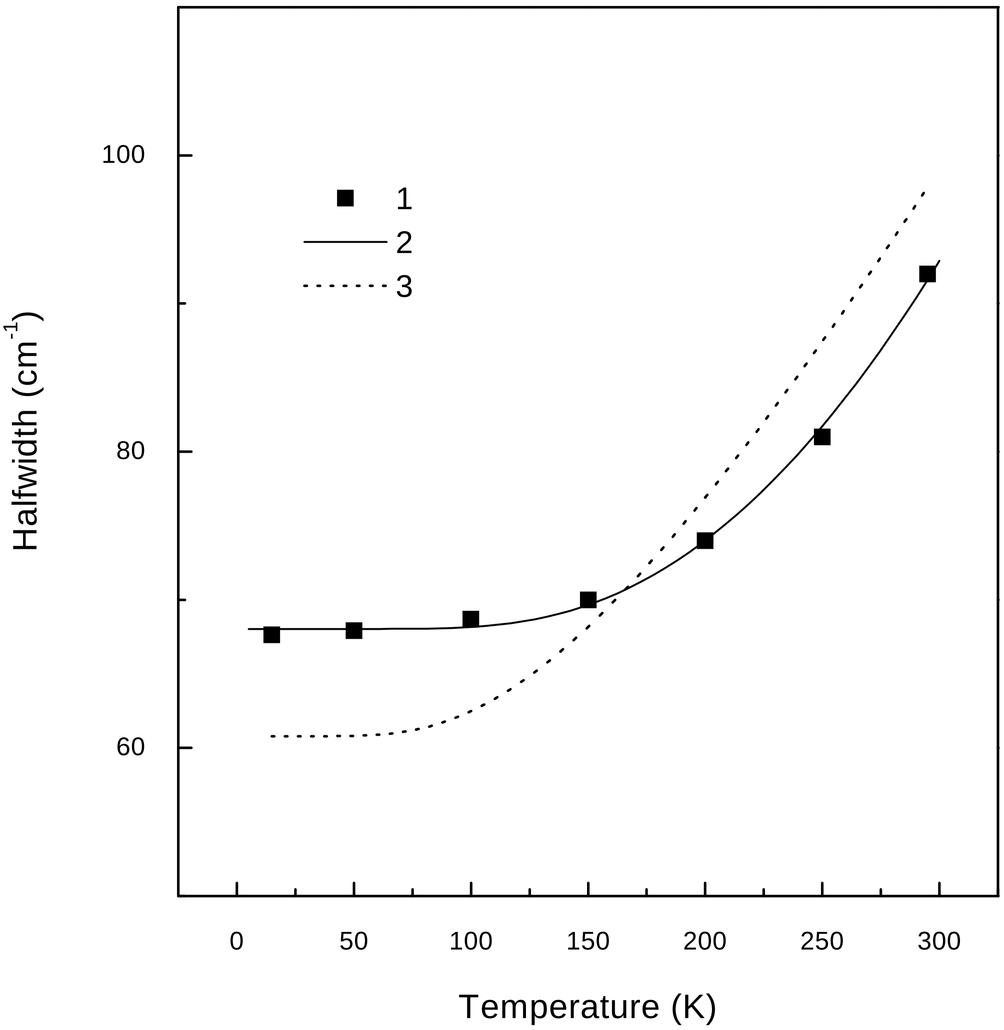


Fig.2. V.M.Burlakov et al., "On a biphononic origin of 1125 cm^{-1} absorption band in cuprous oxide"



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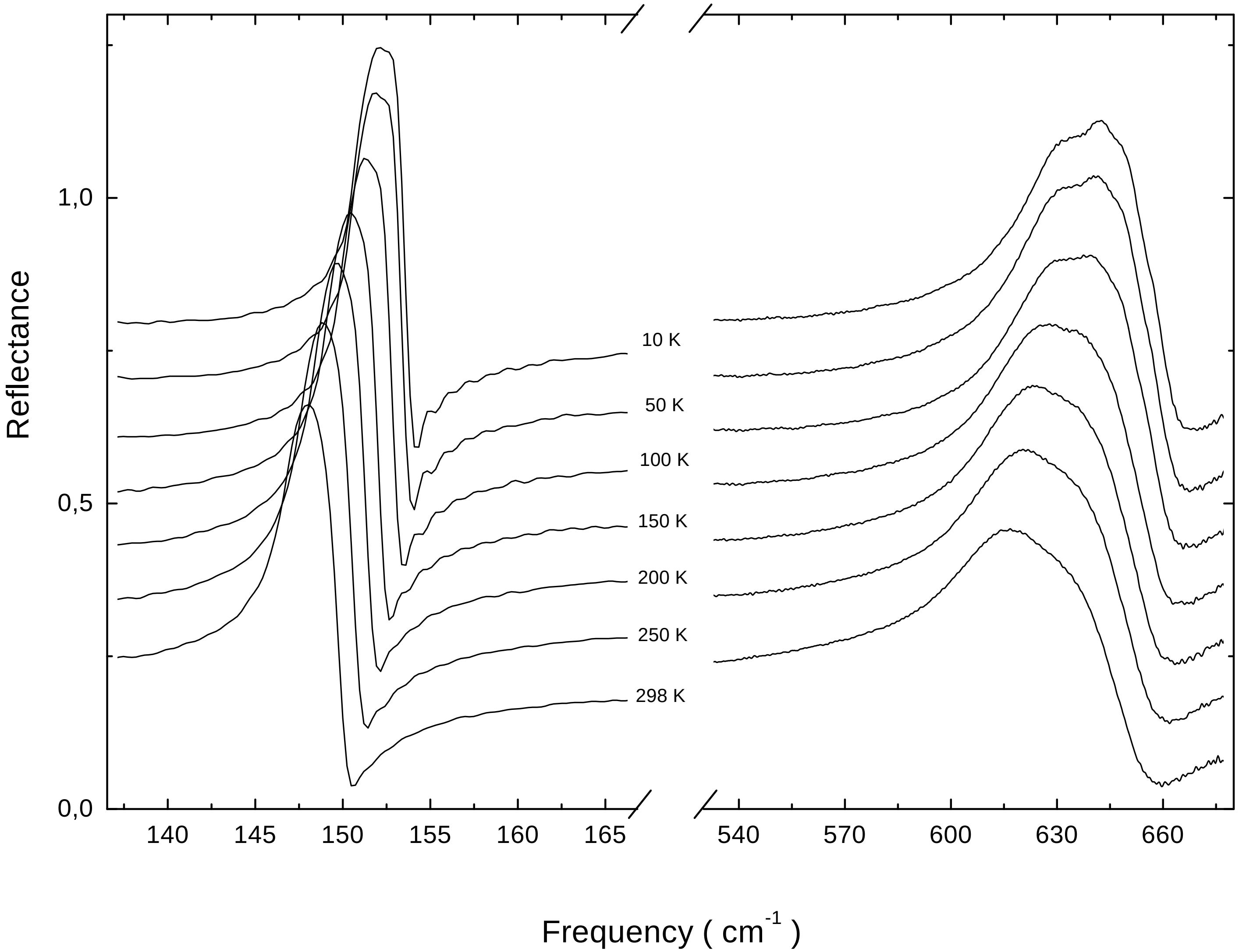

Fig.4. V.M.Burlakov et al., "On a biphononic origin of the 1125 cm^{-1} absorption bands in cuprous oxide"

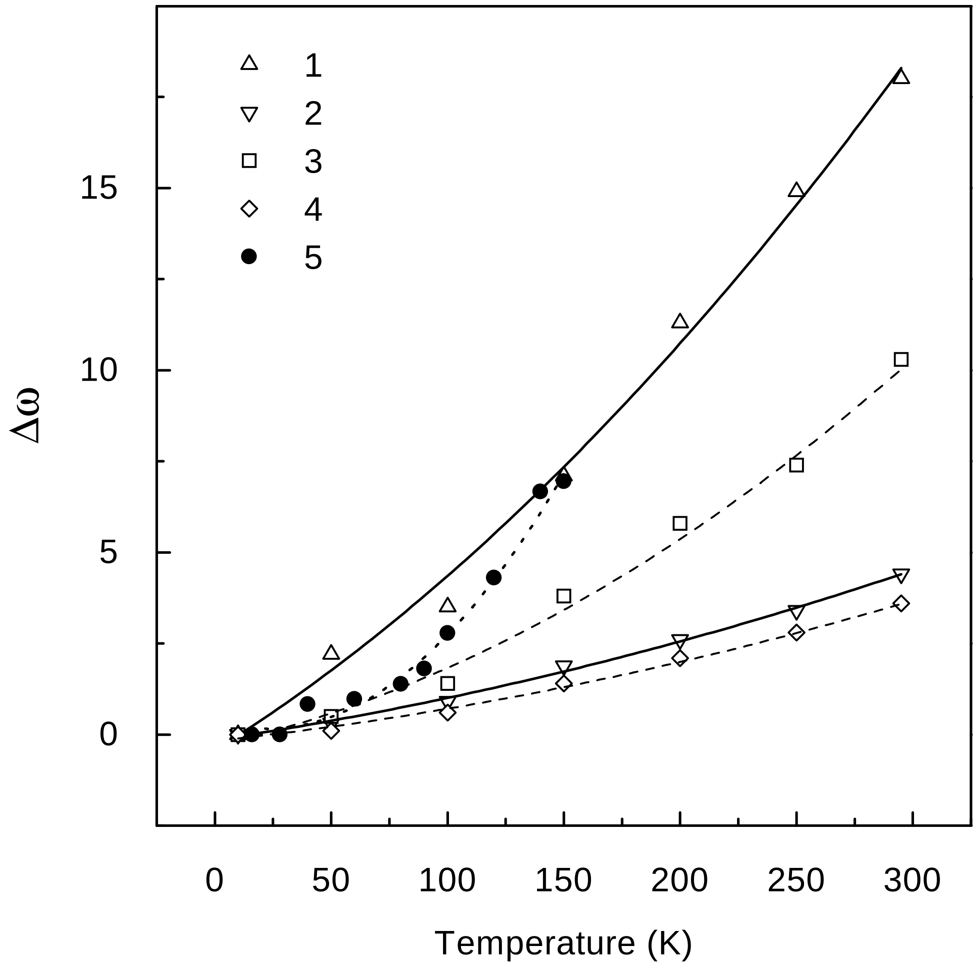

Fig.5. V.M.Burlakov et al., "On a biphononic origin of the 1125 cm^{-1} absorption bands in cuprous oxide"